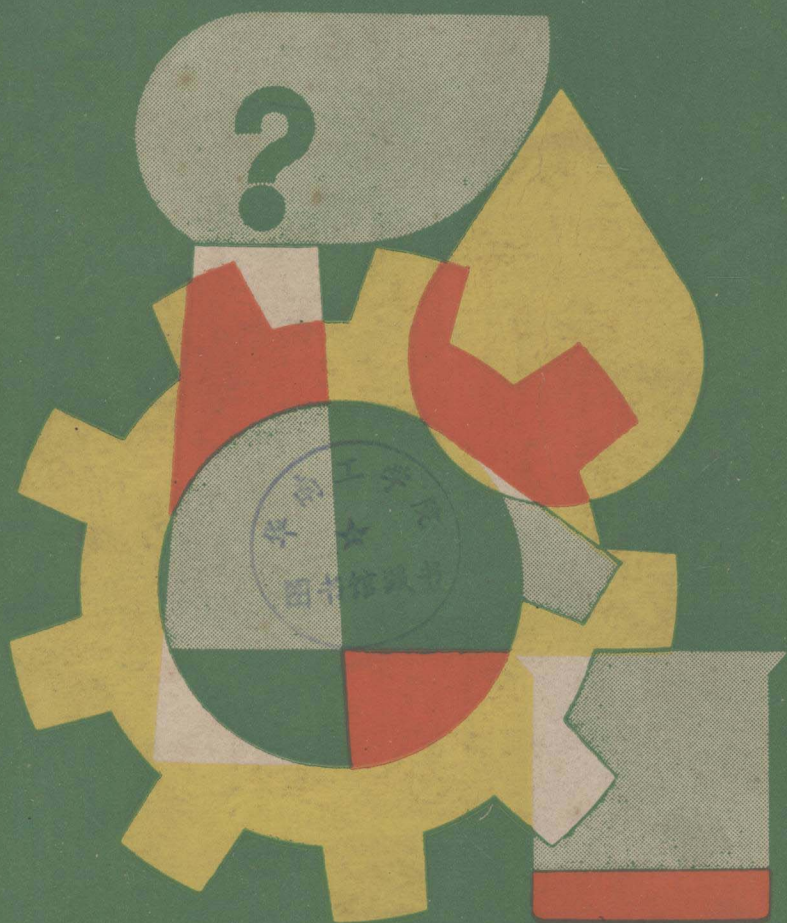


A COURSE IN INDUSTRIAL CHEMISTRY



Ayyangar □ M. V. Hegde □ A. J. Mukhedkar
Narasimhan □ P. G. Pol □ A. C. Ranade

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(Part One)

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A COURSE IN

(Part One)

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Preface

Although it has been evolved from the basic principles underlying the main limbs of chemistry, such as physical-, organic-, inorganic-, and biochemistry, industrial chemistry forms a separate branch by itself. In a technological age, where most industrial processes involve the use of chemical principles, the importance of industrial chemistry cannot be over-emphasised. Therefore, it is heartening to note that Industrial Chemistry has become a part of the syllabus at the undergraduate level.

There is as yet no suitable book for the undergraduate level describing the industries operating under the conditions obtaining in developing countries. This has prompted us to write this book. It is obvious that it is not possible for any single person to give satisfactory treatment to the wide-ranging industries based on different principles. We hope our readers will appreciate our combined effort.

As it is not possible to cover a complete course on Industrial Chemistry in one semester, the book is written in parts so that it is convenient for the undergraduate student to study each part within a period of about forty lectures. The selection of topics in Part I is not entirely arbitrary. The industries involving processes which are comparatively simpler are included in Part I.

We have covered various aspects of each industry, such as raw materials, physico-chemical principles underlying the manufacturing process, industrial operations, economics of the industry, and the pollution problem. We have tried to make the discussion as simple and easy as possible. Illustrations, diagrams and exercises will, we hope, make the book more useful.

If this book helps the student to discover his inclination towards a career in a particular industry and stimulates his desire for more knowledge about it, we shall feel amply rewarded.

Any suggestions for the improvement of the book in its next edition are most welcome.

N. R. Ayyangar

M. V. Hegde

A. J. Mukhedkar

N. S. Narasimhan

P. G. Pol

A. C. Ranade

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1

SUGAR

M. V. HEGDE

1.1. DEFINITION AND CLASSIFICATION

Sugar belongs to a larger family called Carbohydrates.

Carbohydrates are polyhydroxy aldehydes, polyhydroxy ketones or compounds that can be hydrolysed to them. A carbohydrate that cannot be hydrolysed to simpler compounds is called a monosaccharide. A carbohydrate that can be hydrolysed to two monosaccharides is called a disaccharide. A carbohydrate that can be hydrolysed to many monosaccharides is called a polysaccharide.

The monosaccharides (e. g. glucose and fructose) and disaccharides (e. g. sucrose) are all soluble in water and have a sweet taste and are classified under the collective name sugar. The polysaccharides (e. g. cellulose, glycogen and starch) are no longer soluble in water and have also no sweet taste.

Depending on the number of carbon atoms, a monosaccharide is called triose, tetrose, pentose or hexose. The prefix aldo or keto is used to indicate the presence of an aldehyde or a ketone group in the sugar.

All monosaccharides are reducing sugars. They reduce Fehlings and Benedict reagents. Most disaccharides are also reducing sugars. Sucrose (common table sugar) is a notable exception.

1.2. ROLE OF SUGARS IN THE BIOLOGICAL ENERGY CYCLE

As shown in the Fig. 1.1, there is a massive cycling of chemical energy between the plant and the animal world. Sugars play a central role in this cycle.

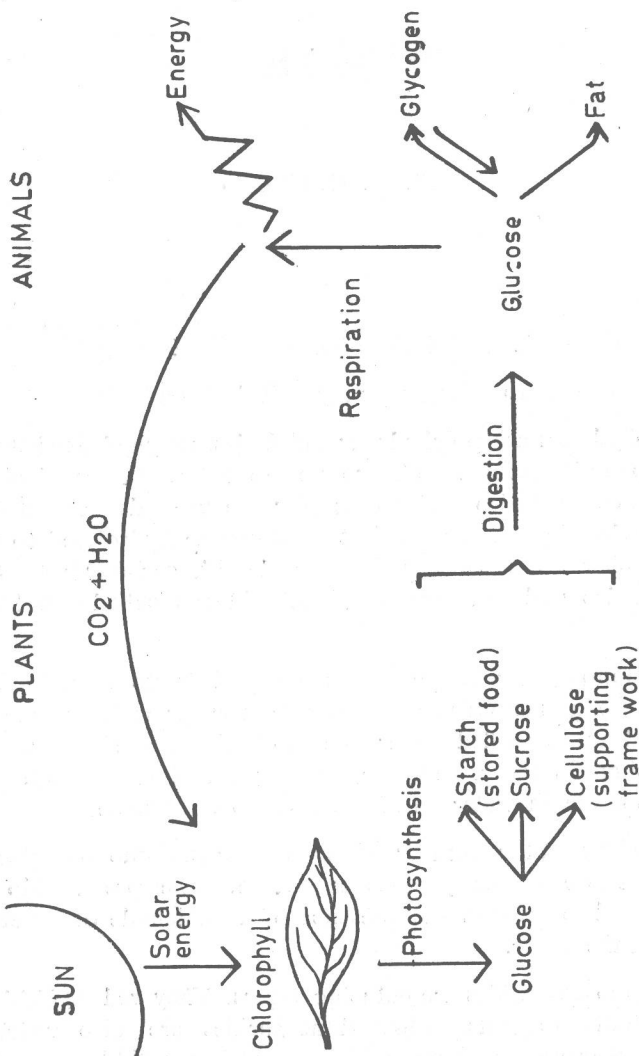
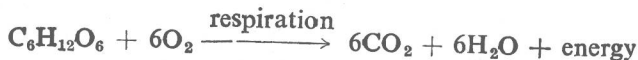


Fig. 1.1 : Role of sugars in the biological energy cycle

In photosynthesis, the energy from the sun is used in the presence of chlorophyll to form sugars from carbon dioxide and water.



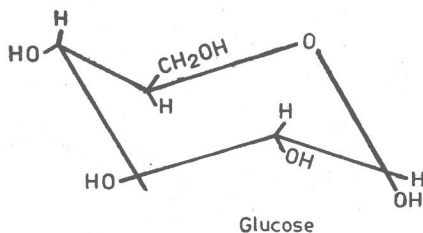
In respiration, the reaction is roughly reversed, and sugars are oxidised to carbon dioxide and water, and the energy is released.



The above simple equations fail to indicate the many steps that are involved in photosynthesis and in respiration. There are many energy releasing steps in the oxidation of glucose to carbon dioxide and water. Not all the energy released is made available for the metabolic functions of the cells. Half of it is lost as heat and only half is used in recharging ADP (adenosine diphosphate) to ATP (adenosine triphosphate), the cellular energy carrier. Thus sugars form the chief source of energy for the living systems.

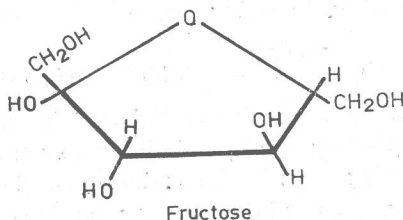
1.3. STRUCTURES OF SUGARS

1.3.1 Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) occurs abundantly in nature as free sugar as well as in combined forms. Its synonyms, blood sugar, grape sugar, corn sugar for glucose are indicative of its wide distribution in nature. Glucose is by far the most important monosaccharide. The structure of glucose is shown below. It has six carbon atoms. Although it has an aldehyde group, this is masked in the cyclic structure.



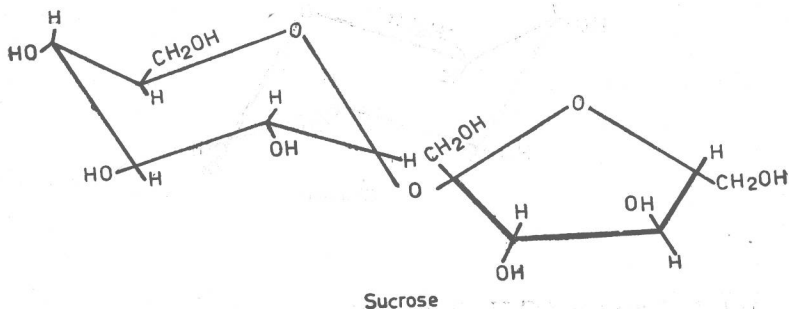
1.3.2 Fructose ($\text{C}_6\text{H}_{12}\text{O}_6$) which occurs in many fruits and in honey as free sugar, is also found in nature in chemical

combination, for example, as in sucrose, which is composed of fructose, and glucose, and in inulin, the polyfructosan, found in many plants. Fructose is the sweetest common monosaccharide. The structure of fructose is shown below.



1.3.3 Sucrose ($C_{12}H_{22}O_{11}$) is the common table sugar, obtained from sugar cane and sugar beet. Of organic chemicals sucrose is produced in the largest amount in pure form.

Sucrose is a disaccharide consisting of glucose and fructose. The monosaccharidic components are condensed at their glycosidic groups with α configuration for glucose and β configuration for fructose. The glucose component is bound in its pyranosidic form while the fructose shows furanosidic form. In agreement with these facts, the exact chemical name of sucrose is α -D glucopyranosyl β -D fructo furanoside the structure being



1.4. CHARACTERISTIC PHYSICAL PROPERTIES OF SUCROSE

1.4.1 Solubility : Sucrose is very soluble in water. Its solubility increases with an increase of temperature. The solubility of sucrose in water is influenced by other dissolved substances.

Table No. 1.1

SOLUBILITY OF SUCROSE IN WATER AT DIFFERENT TEMPERATURES

Temperature, °C	g of sucrose per 100 g of water
0	179.2
20	203.9
40	238.1
60	287.3
80	382.2
100	487.2

A saturated sucrose solution gets super-saturated when it is cooled or when water is evaporated. Super-saturated solutions are metastable, the excess of sucrose is forced out of solution, and sucrose crystals are formed. It is by this process that sucrose is obtained in sugar factories.

1.4.2 Properties of Sucrose Crystals : Crystals of sucrose are monoclinic hemimorphic in nature. The crystals have a prismatic habit. Impurities have a remarkable influence on the form and habit of the crystals. Pure sucrose crystals are transparent and colourless, and melt at 185 to 186°C.

1.4.3 Density of Aqueous Solution : Density of sucrose solution has a set relation to the concentration as shown in Table No. 1.2

The hydrometers are routinely used in sugar factories to determine the concentration of sucrose in fairly pure sugar solutions.

1.4.4 Refractive Index : Light refraction is influenced by the concentration of sucrose in solution as shown in table No. 1.3,

Table No. 1.2

DENSITY OF AN AQUEOUS SOLUTION OF SUCROSE AT 25°C

Concentration, g of sucrose per 100 g of water	Density at 25° g/ml
0	0.997
10	1.036
20	1.079
30	1.125
40	1.174
50	1.227
60	1.283
70	1.344

which gives refractive indices of sucrose solution at sodium light. Determination of refractive indices for the estimation of sugar is the preferred method.

Table No. 1.3

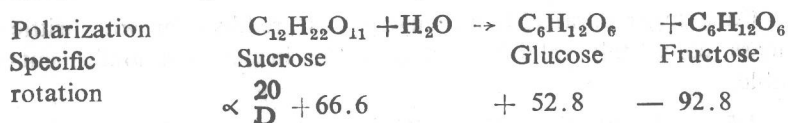
REFRACTIVE INDEX OF AN AQUEOUS SOLUTION OF SUCROSE

Concentration, g of sucrose per 100 g of water	Refractive index at 20° using Sodium D-line
0	1.333
10	1.348
20	1.364
30	1.381
40	1.399
50	1.420
60	1.441
70	1.465

Refraction caused by beet and cane juice impurities is similar to that caused by sucrose. Thus the concentration determined

by the refractometer in impure solutions is not the concentration of sucrose but approximately that of the total dry substance.

1.4.5 Optical Activity : As a consequence of the asymmetric carbon atoms in the sucrose molecule, sucrose solutions rotate the plane of polarized light. When the pure sucrose solution is hydrolysed, a change in the rotation of polarized light is observed according to the following reaction :



The products, a mixture of glucose and fructose are called invert sugar on hydrolysis, the polarization of the pure sucrose 66.6 (+ to the right) now reads -20 (- to the left) for the resulting mixture

$$\frac{+ 52.8 - 92.8}{2} = - 20.0$$

During hydrolysis the optical rotation changes from positive to negative and hence the reaction is called inversion. The losses of sucrose, in sugar factories as a result of inversion should be well guarded. If the acidity is too high, inversion occurs. This not only causes destruction of sucrose, but also results in other losses due to the fact that invert sugar holds considerable sucrose which cannot be crystallised out. The inversion may also be brought about by the enzyme invertase. Loss due to enzymatic inversion can be kept to the minimum by suddenly heating the juice to high temperatures to inactivate the enzyme.

1.5. CHEMICAL PROPERTIES

1.5.1. Reducing Properties of Sugars : Reducing sugars are characterised by their ability to reduce the copper ion contained in Fehling's solution or silver ion in ammoniacal silver nitrate solution. Sucrose is a non-reducing sugar, on hydrolysis, however, it gives glucose and fructose which are reducing sugars. The chemical methods for the determination of sugars are based on reducing properties.

1.5.2. Caramelisation : Caramelisation is the browning of sugar. When sugar is heated to 200°C a dark coloured mate-

rial is formed. This is apparently due to dehydration and condensation reactions of the heated sugars. Caramels are formed from sucrose, as well as from glucose and fructose. In commercial process high temperatures are avoided to prevent or minimise caramelisation. The reaction occurring in caramelisation is probably as follows :



Cane sugar caramel is an amorphous reddish brown brittle mass, completely soluble in water, bitter in taste and nonfermentable.

1.5.3. Sucrate Formation : With alkali sucrose forms sucrate, $\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{K}$, which is alkaline. The sucrate of lime is important in sugar technology. The mono and disucrate of lime are soluble in water at normal temperature. They are decomposed by CO_2 . On boiling they give tribasic sucrate



1.6. NON-CARBOHYDRATE SWEETENING AGENTS

Sucrose, common sugar, is a natural sweetening agent. Fructose is one and half times sweeter than sucrose, whereas glucose is less sweet than either sucrose or fructose. As these belong to the class of carbohydrates, they have food values and provide energy to living organisms.

The sweetening power of natural sugars has now been surpassed by non-nutritive artificial sweetening agents synthesised from non-sugar starting materials. The trade names, the structures and the relative sweetness of these artificial sweetening agents are presented in table 1.4.

Saccharin finds wide commercial use in the manufacture of tooth powder, toothpaste, beverages and drinks. Saccharin does not have any caloric value. It is excreted in urine. It is widely used by diabetic patients who have less tolerance for glucose. The artificial sweetening agents are not entirely free from poisonous effects, P-4000 and dulcine have been reported to cause liver tumor and can interfere in the production of red blood cells in the body. Except for saccharin other sweeteners have been excluded as food additives.